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AQUEOUS COATING MATERIAL FOR INORGANIC BUILDING MATERIALS

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Abstract

Objective

Aqueous coating material for coating inorganic building materials that easily forms a film having an excellent staining resistance and having an excellent adaptability to expansion and contraction along with excellent resistance against base material cracking.

Constitution

Aqueous coating material for inorganic building materials, characterized by containing a fluoropolymer prepared by carrying out the polymerization of a monomer mixture--comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and

0-45 wt% of other copolymerizable monomers--and polymer particles having a mean particle size of 30-200 nm; aqueous coating material for inorganic building materials characterized by containing complex polymer particles of a fluoropolymer prepared by carrying out the polymerization of a monomer mixture--comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and 0-45 wt% of other copolymerizable monomers--with an acrylic polymer prepared by carrying out the polymerization of a monomer mixture comprising 40-100 wt% of an alkyl (meth)acrylate and 0-60 wt% of other copolymerizable monomers.

Claims

1. Aqueous coating material for inorganic building materials, characterized by containing a fluoropolymer prepared by carrying out the polymerization of a monomer mixture--comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and 0-45 wt% of other copolymerizable monomers--with polymer particles having a mean particle size of 30-200 nm.

2. Aqueous coating material for inorganic building materials, characterized by containing complex polymer particles of a fluoropolymer--prepared by carrying out the polymerization of a monomer mixture comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and 0-45 wt% of other copolymerizable monomers--with an acrylic polymer prepared by carrying out the polymerization of a monomer mixture comprising 40-100 wt% of an alkyl (meth)acrylate and 0-60 wt% of other copolymerizable monomers.

3. Process for the production of aqueous coating material for inorganic building materials, characterized by carrying out the polymerization of a monomer mixture comprising 40-100 wt% of an alkyl (meth)acrylate and 0-60 wt% of other copolymerizable monomers in the presence of a fluoropolymer prepared by carrying out the polymerization of a monomer mixture comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and 0-45 wt% of other copolymerizable monomers.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to an aqueous coating material for inorganic building materials. In particular, it pertains to an aqueous coating material for coating cement, mortar or concrete-finished floors, walls, ceilings or roofs, and to various inorganic building materials used to build floors, walls, ceilings and roofs such as gypsum board, asbestos-slate, asbestos board, precast concrete, lightweight foam concrete, fiber-reinforced concrete, slab slate, asbestos cement calcium silicate board, wood cement board, glass, tile, brick, roof tiles, etc., easily forming films having an excellent climate resistance and staining resistance, and at the same time having an excellent adaptability to expansion and contraction of the base material and resistance against base material cracking.

[0002]

Prior art

Previously, solvent-type coating materials made of vinyl chloride resin, chloroprene rubber, urethane resin, epoxy resin, acrylic resin, etc., and aqueous coating materials made of styrene-butadiene rubber latex, poly(vinyl acetate) emulsion, ethylene-vinyl acetate copolymer emulsion, acrylic resin emulsion, etc., have been coated on inorganic building materials in factories where they are being prepared or assembled or on building sites after they are prepared or assembled. The durability of inorganic building materials has been drastically improved in recent years due to the technical innovations, but in the case of coating materials providing decoration to the surface appearances of these building materials and maintaining their aesthetics, the performance of coating films prepared from them with respect to climate resistance and smear resistance has not necessarily been satisfactory.

[0003]

Aqueous coating materials containing fluoropolymer particles have excellent climate resistance so they require no recoating for a long period of time, at the same time, the heat resistance, gas permeation resistance, electrical insulation, etc., are also excellent. Furthermore, they are different from those solvent-type fluororesin coating materials conventionally used in recent years, so their development has actively been carried out in recent years as a material satisfying social demands such as

environmental protection, resource saving and safety. However, those aqueous coating materials containing fluoropolymer particles developed to date have an inferior film formation and film elongation due to the crystallinity of the fluoropolymer contained, or if the film formation and film elongation are good because the fluoropolymer is amorphous, an inferior smear resistance occurs because the film is soft. Therefore, there was no coating material for inorganic building materials that easily provides a film having excellent climate resistance and smear resistance and having adaptability to expansion and contraction of the base material as well as resistance against base material cracking.

[0004]

Problems to be solved by the invention

Therefore, the objective of this invention is to provide a coating material for inorganic building materials that easily forms a film having an excellent climate resistance and smear resistance, and having an excellent adaptability to expansion and contraction of the base material as well as resistance against base material cracking.

[0005]

Means to solve the problems

Specifically, this invention is to provide (1) an aqueous coating material for inorganic building materials, characterized

by containing a fluoropolymer--prepared by carrying out the polymerization of a monomer mixture comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene, and 0-45 wt% of other copolymerizable monomers (simply called fluoropolymer, below) and polymer particles having a mean particle size in the range of 30-200 nm (called coating material A, below)--and (2) an aqueous coating material for inorganic building materials, characterized by containing complex polymer particles of a fluoropolymer prepared by carrying out the polymerization of a monomer mixture--comprising 50-95 wt% of vinylidene fluoride, 5-50 wt% of hexafluoropropylene and 0-45 wt% of other copolymerizable monomers--and an acrylic polymer prepared by carrying out the polymerization of a monomer mixture comprising 40-100 wt% of an alkyl (meth)acrylate and 0-60 wt% of other copolymerizable monomers (simply called acrylic polymer, below) (called coating material B, below).

[0006]

The fluoropolymer of this invention is prepared as a copolymer of a monomer mixture comprising 50-95 wt%, preferably 60-80 wt%, and optimally 60-70 wt%, of vinylidene fluoride; 5-50 wt%, preferably 5-20 wt%, and optimally 10-20 wt%, of propylene hexafluoride; and 0-45 wt%, preferably 0-35 wt%, and optimally 10-30 wt% of other copolymerizable monomers. In this invention, if the amount of vinylidene fluoride is less than 50 wt%, the smear resistance is poor; on the other hand, if it is over 95 wt%, the film-formation ability is inferior. If the amount of propylene hexafluoride is less than 5 wt%, the film-formation ability and elongation are inferior, and if it

over 50 wt%, the smear resistance is poor. In the case of inorganic building materials, the surface is uneven, becoming liable to be easily smeared, so the amount of propylene hexafluoride is preferably below 20 wt%. If the amount of the other copolymerizable monomers is over 45 wt%, the smear resistance is inferior.

[0007]

Specific examples of the above other copolymerizable monomers are, for example, fluorine-containing ethylenically unsaturated compounds such as vinyl fluoride, tetrafluoroethylene, trifluorochloroethylene, hexafluoroisobutylene, perfluoroacrylic acid or its alkyl esters, perfluoromethacrylic acid or its alkyl esters, fluoroalkyl esters of acrylic acid or methacrylic acid, perfluoro vinyl ether, perfluoroalkyl vinyl ether, etc.; non-fluorine-containing ethylenically unsaturated compounds such as cyclohexyl vinyl ether, hydroxyethyl vinyl ether, etc.; and non-fluorine-containing diene compounds such as butadiene, isoprene, chloroprene, etc. The use of vinyl fluoride, tetrafluoroethylene, hexafluoroisobutylene, and perfluoro vinyl ether is preferable, and the use of tetrafluoroethylene is optimal.

[0008]

The fluoropolymer of this invention can be prepared using emulsion polymerization, solution polymerization, precipitation polymerization, etc., and in this invention, the fluoropolymer

prepared by emulsion polymerization is preferable. The fluoropolymer is dispersed in the form of particles in an aqueous medium, and the dispersion method is not especially restricted. The aqueous medium of this invention may be water or hydrophilic solvents selected from alcohols, ethers, etc., not dissolving the fluoropolymer, and the use of water is preferable. As a method of dispersing the fluoropolymer in an aqueous medium, there are, for example, (i) a method to carry out the emulsion polymerization of monomers in an aqueous medium, (ii) a method to carry out the phase inversion of a solution of the fluoropolymer, (iii) a method of carrying out the precipitation polymerization of monomers and subsequently dispersing polymer particles formed in an aqueous medium, etc. The use of emulsion polymerization among these methods is preferable because the aqueous dispersion of fluoropolymer particles as they are prepared or after adding various additives described later, if necessary is used as coating material A. The fluoropolymer emulsion polymerization is carried out in an aqueous medium of the raw material monomers in the presence of an emulsifier, polymerization initiator, pH adjuster, etc., as described later.

[0009]

As an emulsifier, there are anionic surfactants, nonionic surfactants, and combinations of anionic and nonionic surfactants; in some cases, it is also possible to use amphoteric and cationic surfactants. As an anionic surfactant, there are, for example, sodium higher-alcohol sulfates, sodium alkylbenzenesulfonates, sodium dialkylbenzenesuccinates, sodium alkyl diphenyl ether disulfonates, sodium polyoxyethylene alkyl

ether sulfates, sodium polyoxyethylene alkyl phenyl ether sulfates, etc. The use of sodium lauryl sulfate, sodium dodecylbenzenesulfonate, sodium polyoxyethylene alkyl ether sulfates, and sodium polyoxyethylene alkyl phenyl ether sulfates among them is preferable. As a nonionic surfactant, there are, for example, polyoxyethylene alkyl ethers, polyoxyethylene alkyl aryl ethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, etc. In general, polyoxyethylene nonyl phenyl ether and polyoxyethylene octyl phenyl ether are used. As an amphoteric surfactant, there are, for example, laurylbetaine, sodium hydroxyethylimidazoline sulfate, sodium imidazoline sulfate, etc. As a cationic surfactant, there are, for example, alkylpyridinium chlorides, alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides, alkyl dimethylbenzylammonium chlorides, etc. As an emulsifier in this invention, it is also possible to use fluorine-type surfactants such as a perfluoroalkyl carboxylate, perfluoroalkyl sulfonate, perfluoroalkyl phosphonate, perfluoroalkyl phosphate, perfluoroalkyl polyoxyethylene, perfluoroalkylbetaines, etc. In this invention, perfluoroalkyl-group-containing surfactants are suitably used; in particular, those surfactants containing perfluoroalkyl groups having 9 or more carbon atoms are preferable. In addition, the use of a perfluorocarboxylic acid having 9 or more carbon atoms and its salt, particularly perfluorononionic acid, perfluorodecanoic acid, etc., is preferable. In addition, the use of an ammonium perfluorocarboxylate among perfluorocarboxylic acids and their salts is preferable. The amount of emulsifier to be used per 100 parts by weight of the total amount of monomers is generally 0.05-5 parts by weight, preferably 0.1-2 parts by weight, and

optimally 0.5-1.5 parts by weight to minimize any adverse effects on the water resistance as well as climate resistance while maintaining the desired particle size.

[0010]

As a polymerization initiator, there are water-soluble polymerization initiators such as sodium persulfate, potassium persulfate, ammonium persulfate, hydrogen peroxide, etc., as well as redox-type initiators among these water-soluble polymerization initiators combined with a reducing agent. As a reducing agent, there are sodium hydrogen pyrosulfite, sodium hydrogen sulfite, sodium sulfite, sodium thiosulfate, L-ascorbic acid or its salt, sodium formaldehyde sulfoxylate, ferrous sulfate, glucose, etc. Furthermore, oil-soluble polymerization initiators dissolved in a solvent are also usable. As such an oil-soluble polymerization initiator, there are, for example, 2,2'-azobisisobutyronitrile, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis-2,4-dimethylvaleronitrile, 1,1'-azobiscyclohexane-1-carbonitrile, 2,2'-azobisisovaleronitrile, 2,2'-azobiscapronitrile, 2,2'-azobi(phenylisobutyronitrile), benzoyl peroxide, di-t-butyl peroxide, dilauroyl peroxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, para-menthane hydroperoxide, t-butyl hydroperoxide, 3,5,5-trimethylhexanol peroxide, diisopropyl peroxydicarbonate, t-butyl-peroxy(2-ethylhexanoate), etc. The use of oil-soluble initiators such as 2,2'-azobisisobutyronitrile, benzoyl peroxide, di-t-butyl peroxide and diisopropyl peroxydicarbonate is preferable. The amount of polymerization initiator to be used per 100 parts by weight of

the total amount of monomers is generally 0.1-5 parts by weight. The use of oil-soluble initiators is preferable, considering the climate resistance. If a water-soluble initiator is used, the amount is preferably below 1 part by weight per 100 parts by weight of the total amount of polymers considering the climate resistance.

[0011]

As a chain transfer agent, there are halogenated hydrocarbons (such as chloroform, bromoform, etc.), mercaptans (such as n-dodecylmercaptan, t-dodecylmercaptan, n-octylmercaptan, n-hexadecylmercaptan, etc.), xanthogens (such as dimethyl xanthogen disulfide, diethyl xanthogen disulfide, diisopropyl xanthogen disulfide, etc.), terpenes (such as dipentene, terpinolene, etc.), thiuram sulfides (such as tetramethylthiuram ammonium sulfide, tetraethylthiuram disulfide, tetrabutylthiuram sulfide, dipentamethylthiuram disulfide, etc.), isopentane, alcohols, etc. The use of isopentane, methanol, ethanol, and isopropanol is preferable. The amount of such a chain transfer agent to be used per 100 parts by weight of the total amount of monomers is about 0-10 parts by weight. As a chelating agent, there are, for example, glycine, alanine, ethylenediaminetetraacetate, etc., and as a pH adjuster, there are, for example, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, dibasic sodium phosphate, etc. The amounts of such a chelating agent and pH adjuster to be used per 100 parts by weight of the total amount of monomers are about 0-0.1 part by weight and 0-3 parts by weight, respectively. The

polystyrene-conversion weight-average molecular weight of the fluoropolymer of this invention is generally 1-500,000.

[0012]

The mean particle size of the fluoropolymer particles of this invention is 30-200 nm, preferably 30-150 nm, and optimally 30-100 nm. If the mean particle size is smaller than 30 nm, it is necessary to use a large amount of surfactant, with which the climate resistance is adversely affected, in order to maintain the stability of the particle dispersion; on the other hand, if it is over 200 nm, the sedimentation stability and film formation ability are inferior. In this invention, the mean particle size of the fluoropolymer particles may be set in the above specific range generally using an emulsifier in an amount of 0.2 part by weight or more per 100 parts by weight of the total amount of monomers, preferably 0.2 part or more of a perfluorocarboxylic acid having 9 or more carbon atoms or its salt. The solids content of coating material A of this invention is generally 10-70 wt%, preferably 20-60 wt%. Coating material A may be used alone or 2 or more kinds may be mixed before using.

[0013]

In the coating material for inorganic building materials, the smear resistance, film formation ability, and sedimentation stability are improved by forming polymer particles of the fluoropolymer complexed with an acrylic polymer prepared by carrying out the polymerization of a monomer containing 40-100 wt% of an alkyl (meth)acrylate (called composite polymer

particles, below). The composite polymer particles of this invention have two or more kinds of polymers present in single particles regardless of the presence or absence of any chemical bonding between the polymers. With respect to climate resistance, film formation ability, and particle dispersion stability, the particle structure is preferably not that of the core-shell type. These particles may assume any structure other than the core-shell type, but the use of a homogeneous-type structure is preferable because the restrictions on the usage conditions, especially the drying temperature and time, can be reduced.

[0014]

As a process for the production of such composite polymer particles in this invention, there are methods to prepare particles of either the fluoropolymer or acrylic polymer first, and subsequently carry out the polymerization reaction for the other polymer in the presence of the first polymer particles; carry out the polymerization reaction of monomers to obtain the fluoropolymer and acrylic polymer in the same reactor; and convert the fluoropolymer-containing solution to an aqueous dispersion. In this invention, the method used to carry out the polymerization reaction of a monomer containing an alkyl (meth)acrylate in the presence of fluoropolymer particles is preferable. In this invention, the content of the alkyl (meth)acrylate component in the acrylic polymer is 40-100 wt%, preferably 40-99.9 wt%, and optimally 50-99 wt%. If the amount of alkyl (meth)acrylate is less than 40 wt%, the climate resistance is inferior.

[0015]

As an alkyl (meth)acrylate usable for the production of the composite polymer particles of this invention, there are, for example, acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, hexyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, etc., preferably butyl acrylate and 2-ethylhexyl acrylate, as well as alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, etc.

[0016]

In this invention, the use of an alkyl methacrylate, the alkyl group of which has 1 or 2 carbon atoms, that is, methyl methacrylate or ethyl methacrylate, is preferable with respect to the climate resistance, and considering the film formation ability, the combination of an alkyl methacrylate and alkyl acrylate is preferable. Incidentally, the amount of an alkyl acrylate in the acrylic polymer is generally 5-50 wt%. As a monomer copolymerized with (meth)acrylate in this invention, there are the following examples.

[0017]

(a) Monomers having a multiple number of oxyethylene units as a repeating unit, such as methoxypolyethylene glycol acrylate, methoxydiethylene glycol acrylate, ethoxydiethylene glycol acrylate, methoxytriethylene glycol acrylate, ethoxytriethylene glycol acrylate, phenoxypolyethylene glycol acrylate, methoxypolyethylene glycol acrylate, nonylphenoxypolypropylene glycol acrylate, methoxypolyethylene glycol methacrylate, methoxytriethylene glycol methacrylate, phenoxypolyethylene glycol methacrylate, methoxypolyethylene glycol methacrylate, etc. The use of the following compounds is preferable because they also play the role of an emulsifier required at the time of polymerization: nonylphenoxy polypropylene glycol methacrylate, nonyl-1-propenylphenoxy polyethylene glycol, nonyl-1-propenylphenoxy polyethylene glycol sulfate, octyl-1-propenylphenoxy polyethylene glycol, octyl-1-propenylphenoxy polyethylene glycol sulfate, 2-(nonylphenoxy)-1-(allyloxymethyl)ethoxy polyethylene glycol, 2-(nonylphenoxy)-1-(allyloxymethyl)ethoxypolyethylene glycol sulfate, etc. The amount is preferably 0.1-5 wt%, considering the sedimentation stability.

(b) Ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, maleic anhydride, crotonic acid, etc., especially acrylic acid and itaconic acid, in the amount of 0.1-5 wt%, considering the sedimentation stability

[0018]

(c) Other monomers, for example, amides such as acrylamide, methacrylamide, N-methyl acrylamide, N-methyl methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, N-alkyl acrylamide, N-alkyl methacrylamide, N,N-dialkyl acrylamide, N,N-dialkyl methacrylamide, diacetone acrylamide, diacetone methacrylamide, etc.; acrylates such as 2-hydroxyethyl acrylate, N,N-dialkyl aminoethyl acrylate, glycidyl acrylate, fluoroalkyl acrylate, acetonitrile acrylate, diacetone acrylate, etc.; methacrylates such as 2-hydroxyethyl methacrylate, N,N-dialkyl aminoethyl methacrylate, glycidyl methacrylate, fluoroalkyl methacrylate, ethylene glycol dimethacrylate, diacetone methacrylate, etc.; vinyl ethers such as acrolein, allyl glycidyl ether, etc.; conjugated dienes such as 1,3-butadiene, isoprene, chloroprene, etc.; aromatic vinyl compounds such as styrene, α -methylstyrene, halogenated styrene, divinylbenzene, styrene, etc.; cyanovinyl compounds such as acrylonitrile, methacrylonitrile, etc.; and vinyl alkyl ketones such as vinyl methyl ketone, vinyl ethyl ketone, vinyl isobutyl ketone, etc.

[0019]

The sedimentation stability of the composite polymer particles prepared can be improved if 0.1-5 wt% of an ethylenically unsaturated carboxylic acid among these copolymerizable monomers is used. Furthermore, 0.1-5 wt%, especially 0.2-1 wt%, of a monomer having a low polymerization reactivity is preferably used in the acrylic polymer so that the compatibility between the fluoropolymer and acrylic polymer is

improved by inhibiting the polymerization reaction. As such a monomer having a low polymerization reactivity, there are, for example, acrylates or methacrylates having alkyl groups, such as 2-ethylhexyl, lauryl, stearyl, cyclohexyl, t-butyl, norbornyl, etc., α -methylstyrene, etc. The amount of the fluoropolymer per 100 parts by weight of the acrylic polymer is 10-10,000 parts by weight, preferably 50-5000 parts by weight, and optimally 100-900 parts by weight. If the amount of the fluoropolymer is over 10,000 parts by weight, the effects for improving the smear resistance, film formation ability, and sedimentation stability are small; on the other hand, if it is less than 10 parts by weight, the climate resistance is inferior.

[0020]

The emulsion polymerization for the acrylic polymer in the presence of fluoropolymer particles in this invention is considered to be a type of seed polymerization. The reaction behavior is not necessarily clear, but the polymerization reaction is considered to be carried out while the monomer added is absorbed in general or adsorbed on the fluoropolymer particles, causing them to be swollen. The conditions of this emulsion polymerization are not especially restricted; for example, the reaction can be carried out at a temperature of about 30-100°C in an aqueous medium in the presence of an emulsifier and polymerization initiator for 1-30 h by adding a chain-transfer agent, chelating agent, pH adjuster, organic solvent, etc., if necessary. As an emulsifier, there are anionic surfactants, nonionic surfactants, combinations of anionic and nonionic surfactants, etc.; in some cases, it is also possible to

use an amphoteric surfactant or cationic surfactant. Specific examples of these are the same as those mentioned for the production of the fluoropolymer. In addition, it is also possible to use a reactive emulsifier that is copolymerizable with the acrylic polymer, such as sodium styrenesulfonate, sodium allyl alkyl sulfonate, etc., in this invention. The amount of emulsifier to be used per 100 parts by weight of the acrylic polymer is generally 0.05-5 parts by weight.

[0021]

The polymerization initiator, chain-transfer agent, and chelating agent may be the same as those usable for the production of the fluoropolymer. The use of water-soluble polymerization initiators such as potassium persulfate, ammonium persulfate, sodium persulfate, etc., is preferable. The amount of polymerization initiator to be used per 100 parts by weight of the acrylic polymer is generally about 0.1-3 parts by weight. The amount of chain-transfer agent to be used per 100 parts by weight of the acrylic polymer is in the range of about 0-10 parts by weight. The amounts of chelating agent and pH adjuster to be used per 100 parts by weight of the acrylic polymer are 0-0.1 part by weight and 0-3 parts by weight, respectively. As an organic solvent, there are, for example, methyl ethyl ketone, acetone, trichlorotrifluoroethane, methyl isobutyl ketone, dimethyl sulfoxide, toluene, dibutyl phthalate, methylpyrrolidone, ethyl acetate, etc. The amount of such a solvent to be used is preferably as small as possible within the range not damaging the operation efficiency, accident prevention and safety, environmental safety, and manufacturing safety; specifically, it

is less than about 20 parts by weight per 100 parts by weight of the acrylic polymer.

[0022]

In the case of emulsion polymerization of the acrylic polymer in the presence of fluoropolymer particles, the fluoropolymer particles and acrylic monomer can be added using a method selected from various types. For example, they are ① the total amount of the acrylic monomer is added in a single portion to an aqueous dispersion of the fluoropolymer particles, ② a portion of the acrylic monomer is added to an aqueous dispersion of the fluoropolymer particles to carry out the reaction, with the remaining acrylic monomer being subsequently added continuously or in portions, ③ the total amount of the acrylic monomer is added continuously or in portions to an aqueous dispersion of the fluoropolymer particles, ④ the fluoropolymer particles are added continuously or in portions while carrying out polymerization of the acrylic monomer, etc. The use of method ① or ②, with the initial amount of monomer charged being 50 wt% or more based on the total monomer amount, is preferable. The mean particle size of the composite polymer particles is generally 30-200 nm, preferably 30-150 nm, and optimally 30-100 nm. If the mean particle size is below 30 nm, it is necessary to use a large amount of surfactant, which adversely affects the climate resistance, to maintain the particle dispersion stability; on the other hand, if it is over 200 nm, the sedimentation stability and film formation ability are inferior. The mean particle size of the composite polymer particles is adjustable by suitably selecting the size of the

fluoropolymer particles. In this invention, the solids content of the coating material B is generally 20-80 wt%, preferably 30-70 wt%. Coating material B may be used alone or two or more kinds may be used as a mixture. Furthermore, it is also possible to mix coating material A and coating material B.

[0023]

The coating material for inorganic building materials of this invention can be compounded with various organic additives, if necessary, in the amount of less than 40 parts by weight per 100 parts by weight of the solids content of the coating material. Such additives include, for example, silicone-type defoaming agents, antifreezes such as ethylene glycol, propylene glycol, etc., dyes, organic pigments, dispersants, pH adjusters such as ethanolamine, thickening agents such as hydroxyethylcellulose, polyether urethane, acrylic acid copolymer, etc., wetting improvement agents such as butyl Cellosolve, ethyl Cellosolve, etc., organic fillers, antiseptics, antifungal agents, agents to allow water resistance, antiaging agents, UV absorbents, UV stabilizers, water-soluble solvents, film-formation aids, etc. As a UV absorbent, there are salicylates such as ethyl salicylate, phenyl salicylate, cresyl salicylate, benzyl salicylate, etc.; benzophenones such as 2-hydroxybenzophenone, 2-hydroxy-4-benzyloxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-5-chlorobenzophenone, 2-aminobenzophenone, high-molecular-weight modified benzophenones (such as T-57 from Adeka-Argus), etc.; benzotriazoles such as 2-(2'-hydroxy-5'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-butylphenyl)-5-chlorobenzotriazole,

2-(2'-hydroxy-5'-methoxyphenyl)benzotriazole,
2-(2'-hydroxy-3',5'-dineopentylphenyl)benzotriazole,
high-molecular-weight-modified benzotriazoles (such as Tinuvin 900 and 1130 of Ciba-Geigy), etc.; substituted acrylonitriles such as ethyl-2-cyano-3,3-diphenyl acrylate,
2-ethylhexyl-2-cyano-3,3-diphenyl acrylate,
methyl- α -cyano- β -methyl-4-methoxycinnamate, etc.; nickel complex salts such as 2,2'-thiobis(4-octylphenolate) nickel complex salt, [2,2'-thiobis(4-t-octylphenolate)]-n-butylamine nickel complex salt, etc.; dimethyl-p-methoxybenzylidene malonate; resorcinol monobenzoate; hexamethylphosphoric triamide,
2,5-diphenyl-p-benzoquinone; etc. As a UV stabilizer, there are bis(2,2,6,6-tetramethyl-4-piperidine) sebacate, dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensation product, bis(1,2,2,6,6-pentamethyl-4-piperidyl)
2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonate and high-molecular-weight modified hindered amines (such as MARK IA 57, 62, 63, 67, and 68 of the Adeka-Argus Co. and Tinuvin 292 of the Ciba-Geigy Co.) As a film formation aid, there are aliphatic esters, ethylene glycol or propylene glycol condensation derivatives, ketone solvents, etc., but the use of a two-end etherified dimer or trimer of ethylene glycol or propylene glycol is preferable. In this case, the methyl ether products are preferable, and dimethyl ether products are optimal. Furthermore, the use of isobutylate esters are preferable, and the use of an aliphatic diol monoisobutylate is optimal. Furthermore, the coating material for inorganic building materials may be compounded with inorganic compounds; specifically, pigments such as titanium oxide, iron oxide, carbon, etc.; fillers such as

calcium carbonate, silica, Aerosil, etc. If titanium oxide is used, rutile-type titanium oxide is preferable; in particular, highly pure rutile-type titanium oxide prepared by the chlorine process is optimal. If a dark coating on roof tiles, etc., is required, a carbon dispersion solution may be used in the amount of 0.01-5 parts by per 100 parts by weight of the fluoropolymer particles or composite polymer particles to improve the climate resistance, as well as protection of the base and undercoating.

[0024]

The coating material for inorganic building materials of this invention is especially useful as a protective coating. In this case, it is coated on a substrate, then dried at a temperature that is generally from room temperature to about 200°C. As an application field, there are on-site applications of ordinary drying coating material, coating material for line coatings, etc. Coating material B of the composite polymer particles is excellent as a coating material for line coating; it is dried at a temperature of 50-150°C for 0.5-30 min. As a substrate in this case, there are roof tiles such as slate tiles, cement tiles, etc., ceramic sidings, etc. If necessary, solvent solutions, aqueous solutions, and aqueous dispersions of various polymers may be usable as an undercoating. As an undercoating, an acrylic polymer is generally preferable; in particular, an acrylic polymer having the same composition as that of the acrylic polymer used in coating material B is preferable with respect to the close contact of the coating films prepared. If the undercoatings of coating material A and coating material B of this invention are colored or have shielding effects to achieve

certain aesthetics, the coating material of this invention for inorganic building materials is used as a so-called clear coating. In this case, the coating material or undercoating or both is/are preferably compounded with UV absorbents and UV stabilizers. Furthermore, within the range not causing any adverse effects on the aesthetics of the undercoating, the coating material of this invention for inorganic building materials is preferably compounded with some type of pigment [or is] to be used as a clear color.

[0025]

Application examples

This invention is explained in further detail using application and comparative examples as follows, but this invention is not necessarily limited to these examples alone. Incidentally, the parts and % used are those by weight.

Application Example 1

The content of a 6-L autoclave equipped with an electromagnetic stirrer was sufficiently substituted with nitrogen, 2.5 L of deoxygenated pure water and 25 g of ammonium perfluorodecanoic acid as an emulsifier were charged, and the temperature was raised to 60°C while stirring at 350 rpm. Subsequently, it was charged with a gas mixture consisting of 44.2% of vinylidene fluoride monomer (VdF) and 55.8% of hexafluoropropylene monomer (HFP) until the pressure reached 20 kg/cm²G. Subsequently, the polymerization was initiated by

charging 25 g of a Flon 113 solution containing 20% diisopropylperoxy dicarbonate as a polymerization initiator with a certain nitrogen gas pressure. As the polymerization proceeded, the pressure was reduced; thus, a gas mixture consisting of 60.2% of VdF and 39.8% of HFP was successively added to maintain the pressure at 20 kg/cm²G to continue the reaction.

The rate of polymerization was reduced with the reaction time, so after 3 h, the polymerization initiator in the same amount as that described above was charged with a certain pressure of nitrogen gas, and the reaction was continued for 3 h longer. Subsequently, the system was cooled, the stirring was stopped, and the monomer not consumed in the reaction was released to stop the reaction. The solids content of coating material A prepared as described above was 30.5%, and the mean particle size measured by an Ohtsuka Denshi PHOTON CORRELATOR Model LPA-3000S was 51 nm. Furthermore, the composition ratio of the monomers determined by ¹⁹F-NMR was VdF/HFP = 60/40. The film formation ability was evaluated using a Rigaku Kogyo Minimum Film Formation Temperature Meter and by measuring the minimum film formation temperature, which was the temperature at which the film was not peeled off by rubbing with the fingers. The smaller the value, the easier the film formation. Furthermore, the tensile yield elongation and tensile yield strength were measured for the film prepared by drying at a temperature of 20°C over the minimum film formation temperature for 30 min and pressing with a pressure of 0.5 MPa at the same temperature using No. 2 0.5-mm test pieces and the method in JIS K 7127. The higher the value, the better the adaptability to expansion and contraction of the base material as well as the resistance against base material cracking. The results obtained are summarized in Table I.

[0026]

Application Example 2

The same procedures as those used in Application Example 1 were carried out to obtain coating material A consisting of 62% of vinylidene fluoride, 15% of propylene hexafluoride, and 23% of tetrafluoroethylene, having a mean particle size of 98 nm.

[0027]

Table I

①		②		②	
実 施 例		1	2	比較例 1	比較例 2
③	平均粒子径 (nm)	51	92	97	320
⑤	④ 最低造膜温度 (°C)	19	98	133	45
⑥	④ 引張降伏伸び (%)	200	190	48	23
⑦	④ 引張降伏強さ (MPa)	4.1	7.8	4.9	3.8

Key: 1 Application Example
 2 Comparative Example
 3 Mean particle size
 4 Results
 5 Minimum film-formation temperature
 6 Tensile yield elongation (%)
 7 Tensile yield strength (MPa)

[0028]

Comparative Example 1

The same procedures as those used in Application Example 1 were carried out to obtain coating material A consisting of 72% of vinylidene fluoride and 28% of tetrafluoroethylene, having a mean particle size of 97 nm.

Comparative Example 2

The same procedures as those used in Application Example 1 were carried out, except that the amount of ammonium perfluorodecanate was changed to 0.2 g to obtain coating material A consisting of 62% of vinylidene fluoride, 15% of hexafluoropropylene, and 23% of tetrafluoroethylene, and having a mean particle size of 320 nm. From the results obtained, coating material A of this invention was found to be excellent with respect to film formation, elongation, and strength.

Application Examples 3-9

The content of a 7-L separatory flask was substituted with nitrogen, charged with the fluoropolymer aqueous dispersion (as prepared in Application Example 1) in Application Example 3 and that (as prepared in Application Example 2) in Application Example 4, and later in the amount of 150 parts as a solid and 3 parts of ammonium 2-(1-allyl)-4-nonylphenoxy polyethylene glycol sulfate, then the temperature was raised to 75°C. Subsequently, the monomer mixture shown in Table II (or water in some cases)

was added, then the mixture was stirred at 75°C for 30 min. Subsequently, 0.5 part of sodium persulfate was added, then the polymerization reaction was carried out at 85-95°C for 2 h. After the reaction, the mixture was cooled to stop the reaction and to obtain an aqueous dispersion of composite polymer particles. The film formation ability, elongation, and strength were evaluated similarly to Application Example 1. Furthermore, to 30.8 parts of a white pigment dispersion prepared by carrying out the preliminary stirring of 65 parts of titanium oxide CR-97 manufactured by Ishihara Sangyo, 5.2 parts of BYK CHEMIE pigment dispersant Disperbyk 182, 1.3 parts of Sunnopco defoaming agent SN-113, 15.1 parts of ethylene glycol, and 13.4 parts of water in a stirring vessel equipped with 3 blades for 30 min, then dispersion in a Seki Pepapio table-top sand mill for 30 min, the aqueous dispersion of composite polymer particles prepared in the amount of 80 parts of the solid and 8 parts of triethylene glycol dimethyl ether were added to obtain coating material B. This coating material B was applied on a slate roof tile using a 150- μ m spacing applicator, then dried at 80°C for 30 min, then the procedure of JIS-K5400, 9·8·1 was used to carry out a test with a sunshine carbon arc type of climate resistance tester. The proportion of blisters on the sample after irradiation of 3,000 h to that before irradiation (%) was evaluated, and the results were graded according to the following standards.

O: 100-80%

Δ : 79-40%

X: 39% or less

Coating sample plates prepared similarly were exposed at the Yokkaichi plant of Nippon Synthetic Rubber Co., Ltd. by maintaining in the southwest direction and at a 45° angle from

the horizontal plane to measure the lightness difference (ΔL^*) after 1 month of outdoor exposure; the smear resistance was graded according to the following standards.

O: less than 5

Δ : 5-10

X: over 10

Furthermore, to evaluate the adaptability to contraction and expansion of the base material as well as resistance against base material cracking, in an overall manner, a test to carry out dipping in water at 20°C for 18 h, holding in a low-temperature tank at -20°C for 3 h, and retaining in an isothermal tank at 50°C for 3 h as one cycle was carried out; the number of cycles required for the coated surface to show cracks was measured to evaluate the resistance against the heating-cooling cycle. The higher the value, the better the resistance against the heating-cooling cycle. Such evaluation results are shown in Table II.

[0029]

Table II

① 実施例	3	4	5	6	7	8	9
② 含フッ素重合体(部)	150	150	150	1000	150	150	20
③ 単量体混合物 (部)							
④ メタクリレート	75	75	75	75	30	78	75
⑤ 2-エチルヘキシル アクリレート	21	21	0	21	66	22	21
⑥ アクリル酸	4	4	4	4	4	0	4
⑦ 水	0	0	0	0	0	0	90
⑧ 平均粒子径 (nm)	72	123	121	103	124	123	138
⑨ 最低造膜温度 (°C)	30	35	67	85	23	36	80
⑩ 引張降伏伸び (%)	230	220	154	200	250	210	123
⑪ 引張降伏強さ (MPa)	6.3	8.1	9.8	7.9	3.9	8.0	11.3
⑫ 耐候性	○	○	○	○	△	△	△
⑬ 耐汚染性	△	○	○	△	△	△	△
⑭ 耐冷熱サイクル性	>10	>10	10	9	>10	10	8

- Key: 1 Application example
 2 Fluoropolymer (parts)
 3 Monomer mixture (parts)
 4 Methyl methacrylate
 5 2-ethylhexyl acrylate
 6 Acrylic acid
 7 Water
 8 Mean particle size (nm)
 9 Minimum film-formation temperature (°C)
 10 Tensile yield elongation (%)
 11 Tensile yield strength (MPa)

- 12 Climate resistance
- 13 Smear resistance
- 14 Resistance against heating-cooling cycle

[0030]

Application Example 9 and Comparative Example 3

The fluoropolymer aqueous dispersion of Application Example 2 was substituted with that of Comparative Example 2 (Application Example 9) or Comparative Example 1 (Comparative Example 3), and the same procedures as those used in Application Example 4 were carried out to prepare aqueous dispersions of composite polymer particles. Those aqueous dispersions of composite polymer particles and fluoropolymer aqueous dispersions of Application Example 2 and Comparative Example 1 were evaluated by the same procedures as those used in Application Example 4. The results obtained are shown in Table III.

[0031]

Table III

	①	②	③	④
	実施例9	比較例3	実施例2	比較例1
⑤ 平均粒子径 (nm)	340	105	92	97
⑥ 最低造膜温度 (°C)	50	74	98	133
⑦ 引張降伏伸び (%)	146	97	190	48
⑧ 引張降伏強さ (MPa)	7.5	8.5	7.8	4.9
⑨ 耐候性	△	△	○	△
⑩ 耐汚染性	△	×	△	×
⑪ 耐冷熱サイクル性	7	3	8	1

- Key: 1 Application Example 9
2 Comparative Example 3
3 Application Example 2
4 Comparative Example 1
5 Mean particle size (nm)
6 Minimum film-formation temperature (°C)
7 Tensile yield elongation (%)
8 Tensile yield strength (MPa)
9 Climate resistance
10 Smear resistance
11 Resistance against heating-cooling cycle

[0032]

Comparative Example 4

To a Japan Synthetic Rubber Co. acrylic emulsion AE314 in the amount of 95 parts as the solids content, 1 part of the white pigment dispersion prepared in Application Example 4, 12 parts of Dainichiseika carbon dispersion EP510 BLACK TR, and 10 parts of triethylene glycol dimethyl ether were added, then the coating and climate resistance evaluations were carried out by the same procedures as those used in Application Example 4. The results were found to be X for both items.

[0033]

Application Examples 10-12

On the coated plate of Comparative Example 4, the aqueous dispersion of composite polymer particles of Application Example 4 with no additives (Application Example 10), 3 parts of

Ciba-Geigy Tinuvin 1130, and 1 part of Tinuvin 292 per 100 parts of the solids content of the composite polymer particles (Application Example 11) or 0.5 part of EP510 BLACK TR (Application Example 12) were coated using the same procedures as those used in Application Example 4, then the climate resistance was evaluated. The results obtained were Δ , 0, and 0, respectively.

[0034]

Effects of the invention

As described above in detail, the coating material of this invention easily provides coating films having climate resistance and smear resistance and has excellent adaptability to expansion and contraction of the base material and resistance against base material cracking. Therefore, it is useful as an aqueous coating material in the case of coating inorganic building materials such as cement, mortar or concrete-finished floors, walls, ceilings or roofs, or gypsum board, asbestos slate, asbestos board, precast concrete, light foam concrete, fiber-reinforced concrete slab slate, asbestos-cement calcium silicate board, woodchip cement board, glass, tiles, bricks, baked roof tiles, etc.